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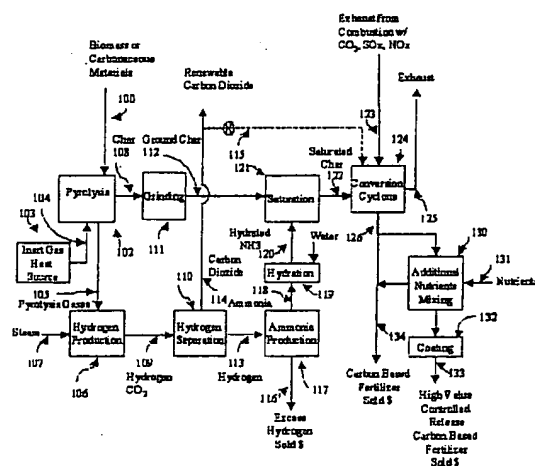
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(54) Title: THE PRODUCTION AND USE OF A SOIL AMENDMENT MADE BY THE COMBINED PRODUCTION OF HYDROGEN, SEQUESTERED CARBON AND UTILIZING OFF GASES CONTAINING CARBON DIOXIDE



(57) Abstract: This invention relates a series of steps to provide an economical production of a carbon based fertilizer and soil amendment made during the capture of greenhouse gases from the combustion of fossil and non fossil fuels. The invention uses biomass and other carbonaceous sources through pyrolytic conversion to gases and charcoal, to allow for the further production of co-products, such as hydrogen and ammonia. The invention also relates to the combination of hydrated ammonia, combustion flue gas exhaust, and charcoal, provide for the conversion of the charcoal into a valued added soil amendment to return essential trace minerals and plant nutrients to the soil. The ability to produce a large volume carbon co-product while removing mandated emissions and producing renewable based hydrogen provides an economic gain to a large number small and large businesses and increase the chance of achieving significant reductions in greenhouse gas emissions.

5        **The Production and Use of a Soil Amendment Made By the Combined  
Production of Hydrogen, Sequestered Carbon and Utilizing Off Gases  
Containing Carbon Dioxide**

10      **Cross Reference to Related Application**

Applicants hereby claim the benefit under 35 U.S.C. Sec. 119(e) of the U.S. Provisional Patent Application No. 60/420,766, filed October 22, 2002, entitled "The Production and Use of a Soil Amendment made by the Combined Production of Hydrogen, Sequestered Carbon and utilizing Off Gases Containing  
15      Carbon Dioxide", which is fully incorporated herein by reference.

**FIELD OF THE INVENTION**

This invention relates to the production and use of a nitrogen enriched carbon based fertilizer and soil amendment made during the pyrolytic conversion of  
20      carbonaceous materials which produce charcoal and the reaction of said charcoal with ammonia, carbon dioxide, water and other components generally found in flue gas emissions. The invention also relates to the optimization of that charcoal with mineral and plant nutrients to produce and use the combined materials as a soil amendment and fertilizer. The invention also relates to the use of the material  
25      as a way to economically store carbon and captured greenhouse gases in the soil.

**BACKGROUND OF THE INVENTION**

The increasing anthropogenic CO<sub>2</sub> emissions and possible global warming have challenged the United States and other countries to find new and better ways to  
30      meet the world's increasing needs for energy while, at the same time, reducing greenhouse gas emissions. Recent evidence has shown that melting glaciers, freshwater influxes into the oceans and thinning ice at the North Pole are likely the result on the earth's warming. The National Academy of Sciences report in 2002, on Rapid Climate Change, has detailed evidence that changes in the earth's  
35      climate has occurred very rapidly in the past. Due to the mounting evidence of

5 global warming, nations have wisely sought to work together to reduce potential impacts of greenhouse gas emissions through negotiated agreements, most notably the Kyoto Agreement. The agreement, signed currently by a majority of the planet's nation states, seek to limit greenhouse gas emissions at 1990 levels. However, many are calling for greater reductions. On February 24, 2003, Prime  
10 Minister Tony Blair, one of the United States closest allies, said in a speech, "It is clear Kyoto is not radical enough." and "We know now, from further research and evidence, that to stop further damage to the climate we need a 60% reduction world-wide". This number represents trillions of dollars in goods, services and electrons created through those emissions by businesses that perceive risk and loss  
15 of income of such reductions. However, evidence is mounting that a path does need to be implemented quickly and the quickest way to implement a portion of the global solution is to develop commercial and environmental synergies that reduce risk and potential losses. Solutions that stabilize income potential for the world's business community, establish sustainable methods of growing food, and  
20 help meet the energy demands of the economically developing societies will meet far less resistance than solutions with little corresponding value other than sequestration.

The challenge humanity faces is how to significantly reduce of our non-renewable  
25 greenhouse gas emissions. The use of reforestation is one solution, but that is limited as forest and biomass utilize available soil nutrients, primarily nitrogen.

William Schlesinger, Dean of the Nicholas School of the Environment and Earth Sciences at Duke University noted in 2001;  
30 "However, the rate of carbon storage in forests declines as they mature, so the only way by which reforestation programs can continue to sequester carbon over the long term is if they transition into programs that produce commercial biomass fuels; that is, we must replace fossil fuel with biomass energy. It would require reforestation of all the once-forested land on Earth, including that now used for

- 5 agriculture or covered by urban areas, to store 6 PgC/yr—the amount emitted each year from fossil fuel combustion” (Vitousek 1991).

In order to meet these increasing demands, methods have been proposed and are being researched to sequester carbon in the ocean through fertilization and carbon  
10 dioxide uptake (US6,200,530) and through pumping of CO<sub>2</sub> into the ocean (US6,598,407). Other methods, such as injection in coal seams or underground reservoirs are also being researched heavily. All these methods represent an expense except in specific areas where CO<sub>2</sub> can be used for enhanced oil recovery.

15

Many methods have been developed for removing other greenhouse gases and air pollutants such as of nitrogen and sulfur oxides from flue gas exhaust of fossil fuels. Some of these processes result in a byproduct fertilizer, which create a profit center through utilization of the materials. For background purposes, some  
20 related patents that support this approach are discussed here. US 5,624,649, teaches a method for producing potassium sulfate while removing sulfur dioxide from flue gas. US 6,605,263, describes methods for producing ammonium sulfate during the same. US 4,540,554, describes the use of potassium compounds to produce potash fertilizer while scrubbing for sulfur oxides and nitrogen oxides.  
25 US 4,028,087, describes the production of a fertilizer from baghouse sludge-ammonia-acid salts. US 5,695,616, teaches the production of ammonium sulfate and ammonium nitrate via the use of a electron beam and ammonia. In US 6,363,869, potassium hydroxide is to produce potassium nitrate and potassium sulfate from flue gas.

30

The capture of sulfur and nitrogen gases and their conversion into fertilizers does help. They create potent greenhouse gases however it is small in comparison to the impact of carbon dioxide. However, as a fertilizer, they can increase plant growth and help increase natural sequestration. The volume of carbon that has  
35 grown and is growing in the atmosphere means the most direct path is to directly

5    reduce the size of our carbon dioxide pool by capturing and utilizing carbon and  
carbon compounds in long life applications. Capturing carbon while creating a  
value added carbon based fertilizer/soil amendment would help solve the  
problems related to biomass sequestration. It can help restore nutrients that have  
been removed through aggressive harvesting and provide plants with essential  
10    nutrients that allow them to utilize the higher levels of CO<sub>2</sub> in our atmosphere. It  
is also one of the few existing distribution channel (i.e. the farm/agrochemical  
industry), which is paid to move millions of tons of natural and synthetic  
compounds to farms worldwide. However, the most rapid adoption comes with  
profits and income. Therefore, this solution should yield more food, fiber, and  
15    energy than we currently are able to achieve, and it should do it in a way that  
could be sustained for thousands of years without degrading the environment.

Traditional agricultural practices such as land clearing and cultivation of soil have  
led to land degradation, mineralization of soil organic carbon (SOC) and the  
20    subsequent loss of SOC as carbon dioxide (CO<sub>2</sub>) emitted to the atmosphere (Lal  
et al, 1998; Hao et al., 2001). These activities have reduced soil's natural ability  
to grow plant life in abundance. Additionally, the depletion of trace minerals from  
our soils are impacting the health of our ecosphere and risk creating mankind as a  
species depending on a smaller and smaller window of elements to support a  
25    growing world population. This reduction in elemental diversity could have long  
term effects on the future health and development of our species.

The use of carbon-based fertilizers to effect long-term storage of the carbon and  
remove atmospheric carbon dioxide requires that the carbon must be stable and or  
30    convert in the soil to a stable material. The earth has a carbon that meets these  
requirements. That carbon is charcoal. Charcoal makes up a significant  
percentage of our soil. In five representative soil samples, USDA soil scientist  
Don Reicosky, reported that up to 35% of soil carbon was comprised of charcoal.  
What is exciting is that not only is charcoal found in soils in great abundance but  
35    also that it provides substantial value once there.

- 5 Reports of historical use of charcoal as a soil amendment date back over 2000 years to the Amazon rain forest. (Glaser, 1999) Man-made sites, known as "Terra Preta" (black dirt) have been purported to be created by an indigenous people who were able to overcome poor quality soils by adding charcoal. These sites, with their broken pottery and other indicators of human occupation, after a thousand
- 10 years sites are valued today because they out produce non-manmade soils by 3 fold (Mann, 2002). The ability to increase crop yields does not just apply to old charcoal. Steiner, (unpublished) recreated Terra Preta soils in Brazil with fresh charcoal from a local supplier and reported up 280% increases in biomass yields over fertilization alone. His crop yields were even higher. Glaser (1999) reports
- 15 17% increase in rice yields with charcoal additions over a control. Hoshi reports 20-40% increase in plant height and volume with the addition of bamboo charcoal over controls with an optimum at 100g per square meter per year (or 1 ton per hectare or 890lbs/acre). Nishio in studies using commercial charcoal made from bark, found alfalfa growth increases of 1.7-1.9 times over fertilization alone.

20

Relation between charcoal amendments to soil and crop response

Treatment	Amendment (Mg ha <sup>-1</sup> )	Biomass production (%)	Plant type	Soil type
Control	—	100	Pea	Dehli soil
Charcoal	0.5	160	Pea	Dehli soil
Control	—	100	Moong	Dehli soil
Charcoal	0.5	122	Moong	Dehli soil
Control	—	100	Cowpea	Xanthic Ferralsol
Charcoal	33.6	127	Oats	Sand
Charcoal	67.2	120	Rice	Xanthic Ferralsol
Charcoal	67.2	150	Cowpea	Xanthic Ferralsol
Charcoal	135.2	200	Cowpea	Xanthic Ferralsol
Control	—	100	Sugi trees	Clay loam
Wood charcoal	0.5	249	Sugi trees	Clay loam
Bark charcoal	0.5	324	Sugi trees	Clay loam
Activated charcoal	0.5	244	Sugi trees	Clay loam

5 Charcoal is a form of sequestered carbon that will not rapidly decompose and return CO<sub>2</sub> into the atmosphere. It is very resistant to microbial decay. (Glaser 1999; Glaser et al. 2001a). Studies have shown that Terra Preta soils contained up to 70 times more pyrogenic C (charcoal) than the surrounding soils. The hypothesis is that charcoal persists in the soil for centuries due to its chemical  
10 stability caused by the aromatic structure. (Glaser, et al. 2002) The material's chemical structure is resistant to microbial degradation (Goldberg 1985; Schmidt et al. 1999; Seiler and Crutzen 1980). Glaser confirmed the stability by <sup>14</sup>C dating of the soil charcoal with results showing ages of 1,000–2,000 years.(Glaser et al. 2000). Other reports show that charcoal can even be found in highly weathered  
15 environments with carbon dating it back thousands of years. (Gavin, 2002; Saldarriaga et al.1986).

Charcoal has unique physical structures and chemical properties, which if optimized, offer significant value as a soil amendment. Its open porous structure  
20 readily adsorbs many naturally occurring compounds. This property allows charcoal to act as a natural sponge. In crop farming, applied nutrients are rapidly leached below the root zone of annual crops (Cahn et al., 1993; Melgar et al., 1992) however, charcoal can adsorb and hold nutrients at the root level of plants and reduce leaching. (Lehmann, 2000). Charcoal also acts to increase soil's water  
25 holding capacity and increase cation exchange capacity. (Glaser, 1999). Evidence in the Terra Preta soils show that these traits do not diminish significantly with time and therefore new exchange sites are being created, however slowly. Charcoal does breakdown through abiotic oxidation of elemental C to CO<sub>2</sub>, however, under environmental conditions, this process is extremely slow (Shneour  
30 1966). It is known that can fungi and bacteria are capable of de-grading low-rank coals such as brown coal (Fakoussa and Hofrichter 1999). It has been shown (Hofrichter et al. 1999) that extracellular manganese peroxidase is an enzyme of wood-rotting and leaf litter-decaying basidiomycetes capable of degrading macromolecular fractions of brown coal (lignite). As a result of such decay,  
35 reactive products such as phenoxy, peroxy and C-centred radicals are formed

5 which subsequently undergo non-enzymatic reactions leading to the cleavage of covalent bonds, including the fission of aromatic rings. (Glaser, et al. 2002)

Charcoal has the potential to form organo-mineral complexes (Ma et al. 1979), which are found in Terra Preta soils (Glaser et al. 2000). The assumption is that  
10 slow oxidation (biotic and/or abiotic) on the edges of the aromatic backbone of charcoal forming carboxylic groups is responsible for both the potential of forming organo-mineral complexes and the sustainable increase in CEC (Glaser 1999; Glaser et al. 2000, 2001a). From the stand point of carbon sequestration, this means that it is not a permanent removal but from the vantage point of a soil  
15 amendment, it has value now and will continue to add value to soils just as the charcoal added to the Terra Preta soils have done for the last few thousand years.

The open pore structure can provide safe haven from faunal predators for essential symbiotic microbial communities (Pietkien, Zackrisson et al. (1996)). In her  
20 research she investigated microbial communities that would repopulate the ground after a forest fire. In the experiment she prepared four adsorbents, pumice (Pum), activated carbon (ActC), charcoal from *Empetrum nigrum* twigs (EmpCh), and charcoal\* from humus (HuCh) (\*pyrolyzed at 450C). A 25 gram microcosm of untreated humus was covered by 25 grams of the above adsorbents and moistened  
25 regularly with litter extract that contained 170 mg l<sup>-1</sup> glucose, which was included in the total concentration of organic C (730 mg l<sup>-1</sup>). The adsorbents bound organic compounds with different affinities; the adsorbing capacity increased in the order: Pum < HuCh < EmpCh < ActC. After the one-month incubation, the size of the microbial biomass in the adsorbents followed the order EmpCh > HuCh > ActC >  
30 Pum (V, Fig. 1). Activity, measured as basal respiration and rate of bacterial growth rate, were higher in both EmpCh, HuCh than in ActC or Pum. In her analysis, she observes that microbes attached themselves to the charcoal particles and preferentially degraded the adsorbed substrates as with biological activated carbon beds (De Laat et al. 1985, Kim et al. 1997). She concluded that charcoal



5    formed by combustion when moistened with substrate-rich litter extract was capable of supporting microbial communities.

The importance of soil fertility and the need for thriving symbiotic microbial communities cannot be understated. While we do not understand their functions,  
10    the millions of species of fungi, bacteria and other microbiota represent over 15% of all species on the earth. From their roles nitrogen fixing to providing plant defenses, the life below ground represents an ecosystem with thousands to hundreds of thousands of interacting species. (Hanksworth et al, 1992; (Trüper 1992). The development of a carbon based fertilizer should have aspects that  
15    facilitate soil microbe activity. In the production of charcoal, volatile organic species are evolved during the rise in temperature. From 280C to 450C this exothermic process can continue in an oxygen starved environment as is well known to those skilled in charcoal production. These gases (Runkel and Wilke, 1951) as the move through the carbonizing material, are distilled with other  
20    molecules forming both shorter and longer chain molecules. Longer chain molecules have higher dew points. These new compounds then condense to form intraparticle condensates. The continued rise in temperature during the exothermic phase, repeats this process many times before vapor phase molecules leave the char particle. Under increased pressure and subsequent high dew points,  
25    these compounds will remain as additional char (US 5,551,958). Evidence that the condensates provide a source of nutrients for microbial activity from charcoal pyrolysis were demonstrated by the US Geological Survey (Michel, 1999). At temperatures below the highest dew point, specific compounds will necessarily condense. To drive off these remaining molecules require higher temperatures, as  
30    is well known to those who make activated carbons, and when charcoal is halted at lower temperatures, these compounds remain. This evidence supports the results from Pitikein that charred wood perform better as a host site for microbial communities due to the incomplete combustion and available sources of nutrients. There may also be other factors also present which are currently unknown.

35

5 It is well known to those skilled in the art of pyrolysis that above 425°C, that the pipes and reactors remain clear of tar deposits. By removing char from its heated environment at close proximity to this number we can allow a certain amount of volatile organics to remain in the char while still converting the material into a stable form of carbon. The majority will convert into polynuclear aromatic and  
10 heteroaromatic ring systems as structural units. These have been shown to provide charcoals with chemical and microbiological resistance (Haumaier and Zech 1995; Glaser et al. 1998), but not total immunity.

Limited work has been published on optimizing charcoal production for use as a  
15 soil amendment. Glaser, Lehmann and Zech's work in *Biology and Fertility of Soils*, 2002; 35:219-230 present an excellent review of published material. This work reviews the evidence and past work in studying charcoal production and impact as a soil amendment. The Food and Fertilizer Technology Center for the Asian and Pacific Region instructs in a leaflet for farmers on the use of charcoal  
20 that they can experience 10-40% increases and show research results of 138% increases with charcoal plus fertilizer over fertilization alone. The leaflet instructs methods of making rice hull char in an above ground mound charring system. Instructions were limited to charring the material until it was "smoked black" and to not let it turn to ash.

25 The use of charcoal and activated carbon for fertilizers and soil amendments is well known and has been referenced by US 2684295, US 4529434, US 4670039, US 5127187, US 522561, US 5921024, US 6273927, and US 6302396. Each of these teaches that charcoal or activated carbon is a fertilizer component but do not  
30 instruct on its manufacture or optimization for this purpose.

Other patents give more details. US 3259501 teaches the use of an ammoniated and charred rice hulls for fertilizer and US 2171408 teaches the use of sulfuric acid activated carbons for fertilizer due to high ion exchange capacity. No instruction is given on the manufacture of the charcoal. US 3146087 describes a  
35 process for preparing a fertilizer containing water-insoluble nitrogen from wood

- 5 utilizing high pressure and long duration times, however it offers no carbon capture instruction or optimization.

BR 409658 instructs on using charcoal with phosphoric acid, potassium nitrate and ammonia but again no instruction of carbon capture.

10

- BR 422061 teaches that acid groups created in charcoal by chlorine treatment allow adsorption of nitrogen compounds allowing up to 20% available nitrogen. However, the inventor does not relay that this can be developed by a state within a temperature profile of carbonization. He does offer that a gas treatment of chlorine  
15 on a moistened carbonized materials and a treatment on the same by ammonia gas or aqueous ammonia followed by blown air will produce a good ammonium bicarbonate fertilizer but gives no reference to CO<sub>2</sub> or capture mechanism to achieve this product.

- 20 This corresponds to research (Assada et.al, 2002) which showed that lower temperature charcoal produced at 500C adsorbed 95% of ammonia versus charcoal produced at 700C and 1000C which had higher surface areas but only adsorbed 40%. The study noted that acidic functional groups such as carboxyl were formed from lignin and cellulose at 400-500C. (Matsui, et al. 2000;  
25 Nishimya, et. al, 1998). It concludes that charcoals, regardless of source, that form acidic functional groups at these temperatures will preferentially adsorb base compounds such as ammonia and that the chemical adsorption plays the primary role over surface area. This research points to a key ingredient in optimizing a charcoal to act as a nutrient carrier, carbonization conditions.

30

US 5676727 teaches a method for producing slow-release nitrogenous organic fertilizer from biomass. In this process, pyrolysis products obtained from the pyrolysis of biomass use a chemical reaction to combine a nitrogen compound containing the -NH<sub>2</sub> group with the pyrolysis products to form a mixture.

- 5 The process is included for reference but does not mention CO<sub>2</sub> sequestration nor the ability to utilize the process for flue gas cleanup.

US 5587136 instructs on the use of a carbonaceous adsorbent with ammonia in the process of sulfur and nitrogen flue gas removal. Reference is made to it being an active coke but no instructions were provided in its manufacture and no reference to carbon dioxide removal.

US 5630367, provides instructions on converting tires into activated carbons for use as a fertilizer. It instructs using a combustion process with a temperature of 400 to 900 C and preferably 700-800C with air, CO<sub>2</sub> and water vapor. While no specifics are given of yields, the process does detail removal of ash, therefore the temperature of the char is likely to higher than 700 and most of the tire will have been converted to carbon dioxide. The designation of the material as a good carrier for nutrients due to its high cation exchange capacity is a reasonable assumption on the surface but as was shown by (Tryon1948) cation exchange should be converted to cation availability because the sum of the determined cations in charcoal exceeded the CEC by a factor of about 3. Glaser explains that cations in the ash contained in the charcoal were not bound by electrostatic forces but present as dissolvable salts and, therefore, readily available for plant up-take. This increase in "exchangeable" cations, leads to the determination that charcoal CEC measurement is but one component. The mineral ash percentage contained and now concentrated in the charcoal, allow the charcoal to act as a fertilizer itself. Indeed, our microscopic studies of growth in plants in charcoal reveal that root hairs envelope and extend into char particles, probably working in harmony with symbiotic microbiotic communities to extract these nutrients. It is not explained to what extent tire char particles liberated during combustion have trace minerals, however the advantage of returning trace minerals back to the soil from which they were remove via harvest is an important trait of charcoal based fertilizers. The above patent offers that the material may be used as an adsorbent

5 in sulfur and nitrogen flue gas removal however there was no methodology offered as to its use or any particular advantage to the material for this purpose.

US 5,061,467 teaches dry methods from scrubbing sulfur dioxide. Activated charcoal is mentioned but no mention is made to optimize char for ammonia  
10 adsorption or for developing its value as a fertilizer co-product. Gypsum is the only co-product mentioned.

US 6,405,664 instructs on using ammonia liberated from decomposing organic materials. Fly ash to be mixed with dried organics residues as a soil amendment  
15 or additional fuel but the incorporation of dried waste with ammonia is not mentioned.

US 5,587,136, teaches the use of ammonia with a carbon adsorbent but does specify the use for CO<sub>2</sub> removal. Furthermore, the temperature ranges selected  
20 will not support any substantive formation of a carbon based fertilizer and concentrations of ammonia added would not yield conversion percentages needed for this application. The instruction is for choosing a carbon black, which have different physical properties than charcoal and no information is taught on its development or use as a fertilizer.

25 US 6,439,138, teaches that charcoal is shown to capture mercury and heavy organics. No reference is made to utilizing char for capture of CO<sub>2</sub> and the invention teaches that char is preferably formed at 1200F (648C) to 1500 F (815C). Given the small particle size 10,000 microns to 1,000 microns, the  
30 temperature at this size will not optimally produce a material for ammonia adsorption and nor will increase the materials effectiveness as a fertilizer and thus could represent a disposal issue.

US 6,224,839, offers extensive reference to the role played on the adsorption of  
35 NO<sub>x</sub> by carbon in the presence of alkali and alkaline earth metals. This work is

5 incorporated here by reference. The invention discloses the value of char as an adsorbent but offers that the adsorption falls off as sites are filled. No attempt was made to show carbon being replaced as sites were filled, nor to create a value added compound. Instead, the intent was to recycle carbons rather than process them into a fertilizer.

10

In US patent 6,599,118, pyrolysis gasses are added to the combustion gases to remove NOx but the char is burned and no fertilizer is produced.

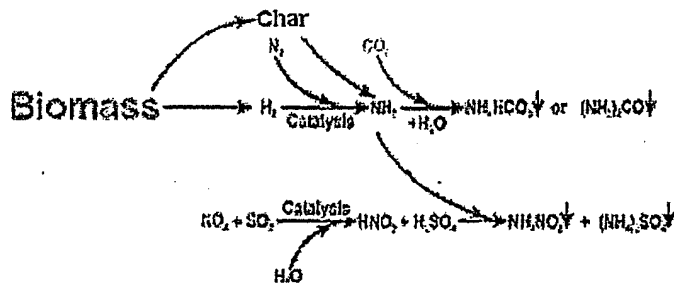
US 4,915,921 teaches the capability of using a coal based activated carbon with ammonia injection for the removal of sulfur oxides and nitrogen oxides at 100-  
15 180C but not carbon dioxide. The carbon was not assumed it would be used as a fertilizer, nor was it optimized.

US 5,584,905, teaches the use household garbage to convert flue gas emissions into a fertilizer. His effort should be admired as he taught ways to increase the  
20 materials value as a fertilizer. His teaches that of ammonia derived from decomposing meats, proteins and fatty acids found in household garbage combining with carbon dioxide to sulfur dioxide to form ammonium fertilizers. While one could envision such a system, the commercial practicality and potential difficulties in gaining environmental permits would prove difficult. He does not  
25 teach the use of char nor the direct use of added ammonia in such a system.

In almost all prior inventions, the amounts of fertilizer generated was so small that the focus has been exclusively of the scrubbing performance. However, a conceptual framework of seeking to increase a sequestering co-product's value  
30 while still conducting essential emissions removal including carbon dioxide has not been demonstrated.

## 5 SUMMARY OF THE INVENTION

It is therefore an object of this present invention to provide an effective soil amendment containing a source of nitrogen or may also include one or more of soil nutrients. Additionally, this material will have properties that provide long term benefit to the user by increasing cation exchange, increasing water holding



- capacity for coarse soils, decreasing nutrient leaching rates, increasing the soil carbon content and a majority of its dry weight represents sequestered carbon.
- 25 Another object is that this material be made during the capture of a  $CO_2$  stream or during the capture process of  $CO_2$  with one or more of the naturally occurring elements and compounds, sulfur oxides, nitrous oxides, mercury, lead and/or heavy metals. A further objective is that a charcoal from the pyrolysis, gasification, and/or partial oxidation of biomass and other carbonaceous materials
- 30 be produced under conditions of this patent and providing for enhanced ability to adsorb ammonia, and decrease nutrient leaching rates. The invention also the object of reducing  $CO_2$  emissions cost of producing the fertilizer and includes the option of utilizing the pyrolysis gas to either be used to produce power, or to be converted to hydrogen and then into ammonia thereby enhancing the total carbon
- 35 sequestered by the system. U.S. Patent No. 6,447,437 B1 provides the path to sequester carbon by scrubbing off gases of power plants and other sources of carbon dioxide with ammonia to produce ammonium bicarbonate or urea. This invention is an improvement in that it takes the production of these carbon-nitrogen compounds and creates them inside the carbon char structure and
- 40 leverages the total amount of sequestered carbon by a factor of 3 to 8 times.

## 5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a method for production of renewable hydrogen and its use in ammonia production, scrubbing and fertilizer production process in accordance with an exemplary embodiment of the present invention.

- 10 Fig. 2 illustrates the design of a simple conversion cyclone system where ammonia is utilized for scrubbing a simulated flue gas component producing a sequestering fertilizer in accordance with an exemplary embodiment of the present invention.

- Fig. 3 provides an illustration of a design to remove CO<sub>2</sub> emissions in industrial  
15 combustion facilities such as a coal-fired power plant by flexible combinations of the synergic processes, the pyrolysis of biomass and or carbonaceous materials and ammonia scrubbing in accordance with an exemplary embodiment of the present invention.

- Fig. 4 provides an illustration representing the environmental, societal and  
20 technical benefits derived from using CO<sub>2</sub> emissions with the carbon capture into fertilizer and the production of renewable energy in accordance with an exemplary embodiment of the present invention.

## DETAILED DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

- 25 The pyrolysis of biomass materials and the steam reforming of the off gases and/or pyrolysis liquids produce significant amounts of hydrogen and a solid char product. Hydrogen, after separation, can be converted into ammonia using the industry standard Haber-Bosch process as the two reactions operate at the same temperature range. The ammonia when combined carbon dioxide (CO<sub>2</sub>) form  
30 ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>), with sulfur dioxide or nitrous oxide and a platinum and nickel catalyst will form HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. These which combined with NH<sub>3</sub> will form as an intermediate of NH<sub>4</sub> HCO<sub>3</sub> and (NH<sub>2</sub>)<sub>2</sub>CO production process, to form additional fertilizer species, (NH<sub>4</sub>)NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The invention described here is the simultaneous production of hydrogen, its  
35 conversion into ammonia, a porous char, the combination of ammonia, and the



5 flue gases of combustion or other high percentage sources of carbon dioxide and the porous char in order to deposition of nitrogen rich compounds in the pore structure of the carbonaceous material. The invention provides the use of this combined porous adsorbent char, enriched with nitrogen compounds, as a slow release fertilizer/soil amendment with also is a novel method for sequestering  
10 large amounts of carbon from the atmosphere. Char makes a perfect media for storing significant quantities of compounds. The combination of nitrogen compounds created in and on the carbon can produce a slow release nitrogen fertilizer with many advantages over traditional ammonium nitrate, urea or liquid ammonia. One of these is that it is less reactive reducing the risk of it being used  
15 a compound for making explosives.

Since both the bicarbonate  $\text{HCO}_3^-$  of  $\text{NH}_4\text{HCO}_3$  and the elementary carbon (C) of the char materials are nondigestible to soil bacteria, they can be stored in soil and subsoil earth layers as sequestered carbons for many years. Therefore, a  
20 combined  $\text{NH}_4\text{HCO}_3$ -char product can not only provide nutrients (such as  $\text{NH}_4^+$ ) for plant growth, but also has the potential to fully utilize the capacity of soil and subsoil earth layers to store both inorganic carbon (such as  $\text{HCO}_3^-$ ) and organic elementary carbon (C). Urea  $(\text{NH}_2)_2\text{CO}$  can also be combined with the char materials to form a similar product. However, the urea production process  
25 generally costs some more energy and has less capacity to solidify  $\text{CO}_2$  than the  $\text{CO}_2$ -solidifying  $\text{NH}_4\text{HCO}_3$  production process (U.S. Patent No. 6,447,437B1). The char materials are also mixable with other nitrogen fertilizer species such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , but those mixtures would not have the benefits of providing bicarbonate ( $\text{HCO}_3^-$ ) to soils. Therefore, the combined  $\text{NH}_4\text{HCO}_3$ -char  
30 product is preferred in realizing the maximal carbon-sequestration potential in soil and subsoil earth layers.

Furthermore, the combined  $\text{NH}_4\text{HCO}_3$ -char product has synergistic benefits. First, the char particles can be used as catalysts (providing more effective  
35 nucleation sites) to speed up the formation of solid  $\text{NH}_4\text{HCO}_3$  particles in the  $\text{CO}_2$ -

5 solidifying  $\text{NH}_4\text{HCO}_3$  production process, thus enhancing the efficiency of the  
CO<sub>2</sub>-solidifying technology. Second, the char materials are generally alkaline in  
pH because of the presence of certain mineral oxides in the ash product. The pH  
value of a typical char material is about 9.8. This alkaline material may not be  
favorable for use in alkaline soils such as those in the western United States while  
10 it is very suitable for use in acidic soils such as those in the eastern United States.  
However, use of  $\text{NH}_4\text{HCO}_3$  can neutralize the alkali of the char materials. When  
the char materials are mixed with  $\text{NH}_4\text{HCO}_3$  of equal weight, the pH of the  
product becomes much better (closer to neutral pH 7). As illustrated in Table 1,  
the pH value of the  $\text{NH}_4\text{HCO}_3$ -char mixture is 7.89, which is significantly lower  
15 (better) than that of the char material (pH 9.85). Therefore, this type of  
 $\text{NH}_4\text{HCO}_3$ -char combined fertilizer will be able to be used in alkaline soils, in  
addition to pH neutral and acidic soils. This type of  $\text{NH}_4\text{HCO}_3$ -char fertilizer can  
be produced either by the char particle-enhanced  $\text{NH}_3$ -CO<sub>2</sub>-solidifying  $\text{NH}_4\text{HCO}_3$   
production process or by physically mixing  $\text{NH}_4\text{HCO}_3$  with char materials.  
20 Figure 1 presents photograph of the  $\text{NH}_4\text{HCO}_3$ -char fertilizer samples that were  
created by char particle-enhanced  $\text{NH}_3$ -CO<sub>2</sub>-solidifying  $\text{NH}_4\text{HCO}_3$  production  
process [marked as "treated char"] and by a physical mixing of  $\text{NH}_4\text{HCO}_3$  and  
char [marked as " $\text{NH}_4\text{HCO}_3$ -char mixture (50%/50%W)"]. Depending on the  
amount of  $\text{NH}_4\text{HCO}_3$  deposited onto the char particles by char particle-enhanced  
25  $\text{NH}_3$ -CO<sub>2</sub>-solidifying  $\text{NH}_4\text{HCO}_3$  production process, the treated char has a pH  
value of 8.76 in this particular sample. The pH of the product can be further  
improved by deposition more  $\text{NH}_4\text{HCO}_3$  onto the char particles by the process.

When the  $\text{NH}_4\text{HCO}_3$ -char product is applied into soil, it can generate another  
30 synergistic benefit. For example, in the western parts of China and the United  
States China where the soils contains significantly higher amount of alkaline earth  
minerals and where the soil pH value is generally above 8, when  $\text{NH}_4\text{HCO}_3$  is  
used alone, its  $\text{HCO}_3^-$  can neutralize certain alkaline earth minerals such as  
[Ca(OH)]<sup>+</sup> and/or Ca<sup>++</sup> to form stable carbonated mineral products such as CaCO<sub>3</sub>  
35 that can serve as a permanent sequestration of the carbon. As more and more

5 carbonated earth mineral products are formed when  $\text{NH}_4\text{HCO}_3$  is used repeatedly as fertilizer for tens of years, some of the soils could gradually become hardened. This type of "soil hardening" has been noticed in some of soils in the western part of China where  $\text{NH}_4\text{HCO}_3$  has been used as a fertilizer for over 30 years. It is also known that this type of soil "hardening" problem could be overcome by  
10 application of organic manure including humus. Char is another ideal organic material that can overcome the "soil hardening" problem because of its soft, porous, and absorbent properties. Therefore, co-use of  $\text{NH}_4\text{HCO}_3$  and char materials together can allow continued formation of carbonated mineral products such as  $\text{CaCO}_3$  and/or  $\text{MgCO}_3$  to sequester maximal amount of carbons into the  
15 soil and subsoil terrains while still maintaining good soil properties for plant growth.

Another embodiment of the invention can be to also add other nutrients to the carbon. The material itself contains trace minerals needed for plant growth.  
20 Adding phosphorus, calcium and magnesium can augment performance and with industry standard coatings create a slow release micro nutrient delivery system.

Another embodiment of the invention can include the processing of the carbon to produce very large pore structures. The material can be used as an agent to  
25 capture watershed runoff of pesticides, and herbicides. By adding a deposition of various materials (example: gaseous iron oxide), the material can be used to capture such compounds as phosphorus from animal feedlots.

Another embodiment for the invention is to use standard industrial processes well known to those skilled in the arts, to use the hydrogen produced, combined with  
30 air and other free nitrogen present in the production process to create the ammonia that will be used as the nitrogen source material.

Based on market demands, these products can be further combined with other  
35 fertilizer species such as potassium, magnesium, ammonium sulfate, ammonium

- 5 nitrate, and micro mineral nutrients such as iron and molybdenum to make more-nutrient-complete compound fertilizers.

#### Example 1

We produced 5 different chars from peanut shells, at different temperatures  
 10 (900°C, 600°C, 500°C, 450°C and 400°C) in a low oxygen environment. In each case, the samples were brought to the target temperature for 1 minute. The samples were taken up to temperature and then allowed to cool. Next the materials were ground and sieved to a particle size less than 30 US mesh and greater than 45 US mesh and prepared 20.0-gram samples. We mixed an aqueous solution of  
 15 48%  $\text{NH}_4\text{NO}_3$  (ammonium nitrate). Each sample was soaked for 5 minutes and then poured through cone filter paper and allowed to air dry for 24 hours. We then poured rinses of 100 ml of tap water (pH8) through the cone filter. The pH of each resulting rinse was measured showing a decreasing pH commensurate with the leaching rates of each material.

20

There was very little difference between the samples except for the one prepared at 400°C. After three or four rinses, the materials, which were carbonized at the higher temperatures, would stabilize at the pH 8 of the rinse material (local tap water). The 400°C char showed very little change and it was only after the 9th  
 25 rinse that it began to drop a bit faster but even after 12 rinses it still had not stabilized.

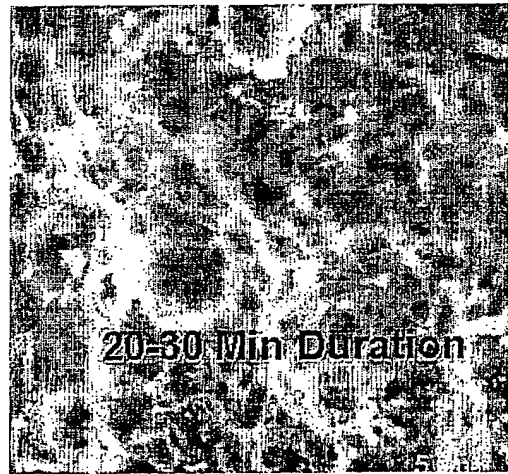
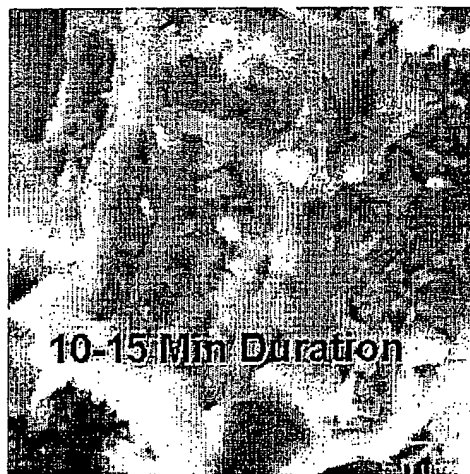
Table 2

CarbonizationpH	pH		Rinses
Temp	Intitail	Final	Required
900 C	9.4	9	4
600 C	9.3	8.8	5
450 C	9.2	8.5	6
400 C	9.1	8.8	12

- 5 The work by Asada on bamboo charcoal demonstrated similar impacts on ammonia adsorption.

#### Example Two

10 While the process can apply to many configurations, this example uses a relatively simple production technique. In this case, we used a mechanical fluidized bed easily adaptable to any gas stream and injected CO<sub>2</sub>, and hydrated ammonia. A 250g charge of 30-45 mesh (0.4mm - 0.6mm), 400 °C char was fed in at regular intervals varying from 15-30 minutes. A higher rotor speed increased the fluidization and suspended the particles until they became too heavy from the  
15 deposition of NH<sub>4</sub>HCO<sub>3</sub> to be supported by fluidized gas flows. The longer durations produced significantly larger particles. At 10-15 minutes the particles ranged from 1.0mm to 2.0mm and between 20-30 minutes they ranged from 3.0 to 6.00mm. The interior of the particles were then examined under a scanning electron microscope. Internal pore structure showed significant formations of  
20 structures of NH<sub>4</sub>HCO<sub>3</sub> at 10-15 minutes. The material produced between 20-30 minutes had completely filled internal pores and cavities.

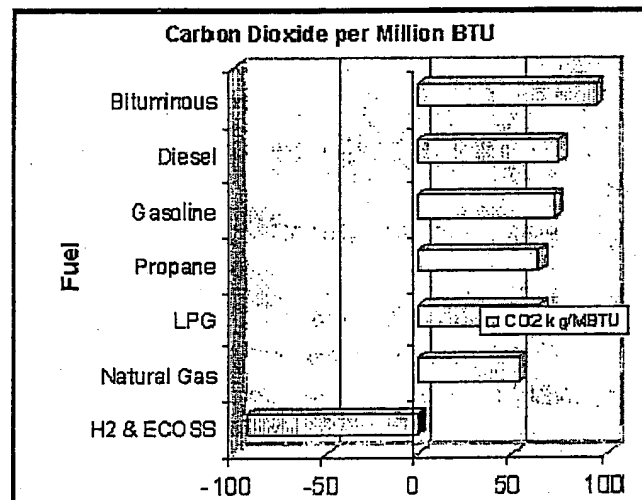


## 5 Global Potential

This chart shows the number of kg of CO<sub>2</sub> per million BTUs of each type fuel. Fossil fuels have a significant carbon cost. Hydrogen used as a fuel with carbon utilization can remove 112kg of CO<sub>2</sub> per GJ of energy used. Current energy use is increasing CO<sub>2</sub> by 6.1 Gt/yr (IPCC). Renewable hydrogen with carbon utilization and CO<sub>2</sub> capture can provide energy with a negative carbon component. To calculate how much negative energy we would need to use at 112kg of CO<sub>2</sub> captured and utilized per 1GJ, to equal the world's 6.1 gigaton CO<sub>2</sub> annual surplus, we divide 6.1Gt/112kg to yield 54Ej. That is approximately what is reported at the world current annual bioenergy consumption (55EJ – Hall)

20

30



The large majority of increases in CO<sub>2</sub> will come from economically developing countries as their burgeoning entrepreneurial populations industrialize. A sustainable technology needs to be able to scale to meet the growing needs of this large segment of the population. Developing an economical size that offers a profitable platform may require certain minimums and it may be that the lower limit of economical production are larger than typical biomass conversion systems. A 1-2 MW facility could be the lower limit yet there are two factors that

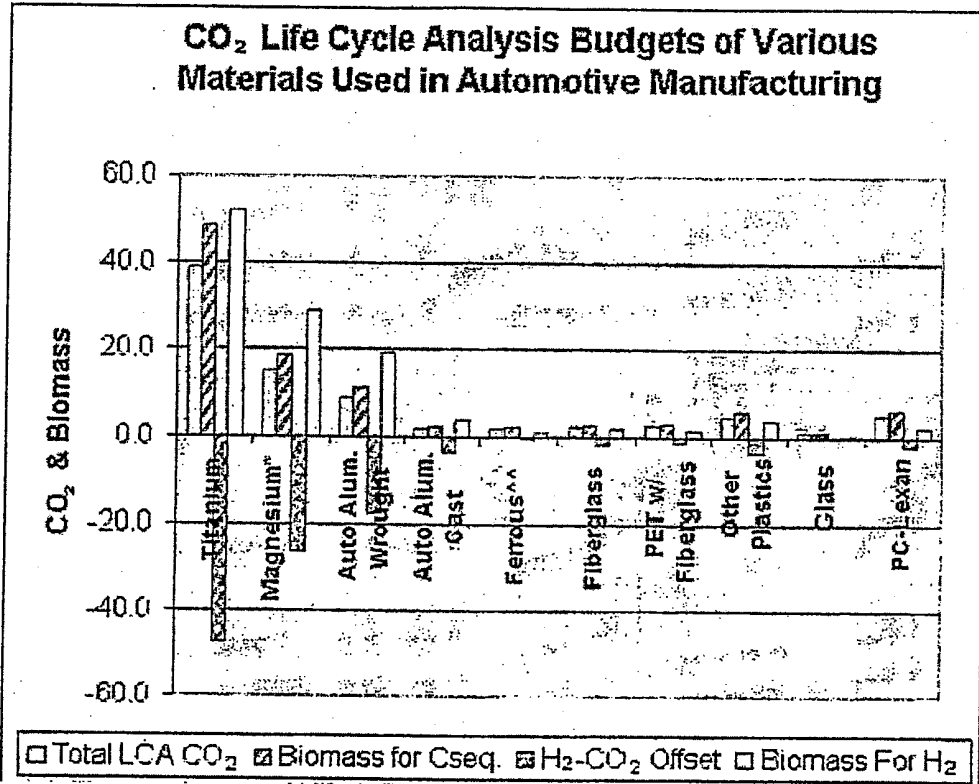
5 are important to note. The first is that the low relative efficiencies required by both the hydrogen separation and the ammonia production may allow a smaller foot print system to be developed using new technologies. Future research efforts in separations technologies and ammonia catalyst could offer developments that lead to systems for even very small farming communities.

10

The second point is that the total hydrogen is approximately three times the maximum that can be utilized in one facility, so every third facility could be designed to accept the charcoal that is produced by two standalone energy systems. This special facility could process all of its hydrogen and the carbon  
15 from two other locations and use existing industrial ammonia manufacturing techniques to create the carbon-fertilizer. If all hydrogen is converted to fertilizer then there is an opportunity to acquire outside CO<sub>2</sub> (34 kg required for each 100 kg biomass processed) and the opportunity to earn revenue from SO<sub>x</sub>, NO<sub>x</sub> removal could provide it with another income stream and help its economics. It  
20 would also fit closely into strategies of developing areas that wish to attract and support GHG emitting manufacturing.

The energy from a total systems point of view could create a viable pathway to carbon negative energy as detailed in the IIASA focus on Bioenergy Utilization  
25 with CO<sub>2</sub> Capture and Sequestration (BECS). The effects shown in the prior graph (Figure 16) (i.e. providing 112kg of CO<sub>2</sub> removal for each GJ of energy used) could allow major manufacturers to offset their carbon costs. The graph in Figure 17 shows various materials used in automobile manufacturing and the life cycle analysis of carbon emissions per kilogram. The second bar in stripes  
30 represents the weight of biomass using this process, which would be required to offset that carbon cost. The third bar, extending down in the checked pattern, shows the amount of sequestered carbon that would be created if the process were used to produce all the energy required for production and the last bar represents the amount of biomass required to meet the energy needs of producing that  
35 amount of the automotive material. In some materials, the amounts needed for

- 5 energy production are less than the amounts needed for carbon offset. This illustrates that energy is just one aspect of GHG production related to materials manufacturing and that methods for offsetting CO<sub>2</sub> release are essential.



(ORNL-2002)

10

The opportunity for economically developing areas with biomass is to utilize their resources to help manufacturers reach carbon-negative status. If the material leaves a factory with a net carbon negative budget, then the behavior of consumerism becomes an agent of climate mitigation and supports economies in side stepping fossil fuel pathways.

15

How large could this method be applied and to what areas of the earth could utilize a concerted effort to reclaim eroded land and increase current farmland production are areas for future research. The positive impact of an increased soil



5 carbon content ultimately leads to increased food and plant yields, further helping to reduce CO<sub>2</sub> buildup. There is very little information on the maximum rates of utilization, though 10,000 kg/ha of char have been used with very positive results and researchers have proposed that as little as 2000 kg/ha could prove beneficial for plant growth. (Glaser, et al. 2002; ICFAC,2002)

10

For a quick test of reasonableness, we saw from above that 1GJ of hydrogen produced and used will represent 112kg of utilized and stored carbon dioxide. Therefore, taking the atmospheric rise of 6.1GT and dividing by 112kg/Gj = 54.5EJ. This number falls amazingly along the 55EJ estimate of the current amount of biomass that is used for energy in the world today.(Hall et al. 1983) While the potential reaches many times this for the future utilization of biomass, this shows that there is a chance that we can be proactive in our approach.

15

#### Technical / Economic Overview and Global Impacts

20 A study of the economics of the ORNL process for NH<sub>4</sub>HCO<sub>3</sub> production from fossil fuel scrubbing was conducted by the University of Tennessee ("UT Study") in 2001. There are also ongoing economic evaluations of renewable hydrogen production from the US National Renewable Energy Laboratory. Those studies can provide the outer framework for this preliminary economic estimate. The UT, examined the economics of producing ammonium bicarbonate in the exhaust stream of fossil fuel combustion. It assumed the use of natural gas to produce ammonia and the subsequent conversion to ammonium bicarbonate. Since this was prior to the use of charcoal inclusion, it did not include any economic gains, which could be attributed to charcoal. Some gains benefit the fossil fuel user.

30 These include a single system for removal of CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub>, no required drying of the final product and offsetting income from fertilizer sales. Optimally, fossil fuel users will partner with fertilizer manufacturers to use their existing market penetration. Fertilizer manufacturing firms, which have been relegated to the sale of commodity goods, can reinvent their product offerings to include

35 service-based delivery of soil fertility and management of soil carbon content.

- 5 Utilizing advances in remote and satellite monitoring technologies and a more in depth local delivery of site specific management techniques, these services will offer a regional advantages which can withstand competition that global commodity chemicals production cannot.
- 10 More gains accrue to farmers as these fertilizers can restore soil carbon content, return trace minerals to degraded lands, increase in cation exchange, water holding capacity, microbial activity and decrease in nutrient leaching which all lead to increases in crop yields. Assumptions of these increases and income derived cannot be made until more detailed yield and cost analysis for the
- 15 amounts of ECOSS utilized, yields of specific crops on representative soils, type of irrigation, and other factors essential to determine farm income. The closed cycle begins with farmers entering into long term contracts to supply energy crops (which can be grown on marginal lands), forestry thinnings and other sources of biomass, which will be required by this soil-food-energy-carbon management
- 20 value chain. These contracts will help establish revenue sources to support effective land, forest and crop management strategies.

Seeing this from a global perspective, this technique simulates the interdependence we find in among organic species in nature. Each role is

25 essential and rewards are evolved through market mechanisms. This diversity in economic gain offers to help restore the growth opportunities to farming, forestry and small rural businesses. Instead of a transfer of wealth, this is a grass roots development of income, which has been literally going up in smoke for the last two centuries. The development of opportunity and broad based growth in

30 entrepreneurial activity, farm operations and businesses that support them, will lead to more stable and predictable income for multinationals, medium and small businesses and lead to an increase in the rural tax base. While this is not a cure all, it moves the world to more sustainable growth strategies.

5 The economic projections of the UT study were based on a market value of the end product at \$2.63/lb atom of nitrogen based on 1999 prices of nitrogen fertilizer. Today's prices are significantly higher due to increased natural gas prices. However, with a target of 20% CO<sub>2</sub> removal, the study concluded that a 700 MW facility would be optimally sized for the economical production of  
10 fertilizer and would yield a after tax ROI of \$0.33. The investment required to meet this level of CO<sub>2</sub> capture was calculated to be \$229 million. The same amount of carbon captured with ECOSSE, where 88% of the target will be met by the carbon contained in the char would only require a production unit one-fifth the size and possibly smaller. Additionally, the system can be much simpler than what  
15 was required to convert 100% of hydrogen produced into ammonia. With this approach, the engineering and construction costs can be significantly reduced. While economics and scale of ammonia production typically favor larger installations, Kyoto reduction targets can be met through smaller facilities where the efficiency is in carbon utilization.

20

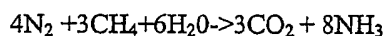
The UT study assumed the world's consumption and demand for nitrogen would become the limiting factor in how much carbon could be captured. The total market for nitrogen in 1999 was 80.95 million tons, which then converted at the power plant targeting 20% reductions in CO<sub>2</sub>, lead to the determination that 337  
25 fossil fuel plants of 237 MW each would meet world fertilizer demand. Their calculations showed that this would reduce the global C output from coal combustion by 3.15%. The study also assumed the use of natural gas to make the ammonia. The total stoichiometric calculation for ammonia from natural gas and the conversion of 8lb-moles of NH<sub>3</sub> into NH<sub>4</sub>HCO<sub>3</sub>, which captures 5 lb moles of  
30 CO<sub>2</sub>. With renewable hydrogen to make ammonia, no fossil fuel based CO<sub>2</sub> is release into the atmosphere and the following is found,  
$$8\text{NH}_3 + 8\text{CO}_2 + 8\text{H}_2\text{O} \rightarrow 8\text{NH}_4\text{HCO}_3.$$

Therefore, renewable hydrogen allows a 1.6 times increase in CO<sub>2</sub> captured per lb-mole of NH<sub>4</sub>HCO<sub>3</sub> produced. Utilizing the study above, a switch to renewable  
35

5 hydrogen would increase carbon capture,  $3.15 \times 1.6 = 5.04\%$ . However, carbon  
closure of biomass energy is not zero but has been calculated (Spath&Mann-1997)  
at 95%. A more accurate number would be  $5.04 \times 95\% = 4.79\%$  reduction in C  
from worldwide coal combustion if renewable  $H_2$  as the source for producing  
ammonia and all the world's N requirements are met from  $NH_4HCO_3$  scrubbed  
10 from power plant exhaust.

As stated before, the total C captured in the combined ECOSS material was 12%  
from fertilizer and 88% from char. Taking the theoretical number of 4.79% and  
equating that to the 12% portion of ECOSS, would mean that the total carbon  
15 capture at 1999 N levels would be increased or leveraged  $100 / 12 = 8.3$  fold or  
reduce total C from coal combustion by  $\sim 39.9\%$ . This leveraged total should be  
seen as a theoretical potential. The factors of increased biomass growth with the  
addition of charcoal as found by Mann (2002), Hoshi(2002), Glaser(2002),  
Nishio(1999) and Ogawa(1983) show increase biomass growth from 17% to as  
20 280% with non-optimized char. The direct utilization of an optimized char plus  
slow release nitrogen/nutrients may allow the increase biomass growth targets  
worldwide. A portion of this increased biomass growth will be converted to soil  
organic matter, further increasing C capture (especially if no-till management  
practices are adopted). Therefore, another bracket in our assessment of this  
25 process is the increase in non-fossil fuel  $CO_2$  capture from biomass growth in  
addition to the leveraged total.

The ability to slow down the release of ammonia in the soil will allow plants to  
increase their uptake of nitrogen. This will lead to a reduction in  $NO_2$   
30 atmospheric release. This potent greenhouse gas is equivalent to 310x the impact  
of  $CO_2$ . The fertilizer industry releases  $CO_2$  during the manufacture of ammonia  
from methane.



The equation illustrates that for each ton of nitrogen produced, 0.32 tons of C are  
35 released, and the 80.95 million tons of nitrogen utilized would represent 26

5 million tons of C. This is a small a small number in relative terms to the amounts released by combustion of coal (2427 million tons- EIA, 2001)

The economics of hydrogen from biomass has been addressed in the 2001 report by Spath et al.(2001). Their conclusion was that pyrolytic conversion of biomass  
10 offered the best economics due in part to the opportunity for co-product production and reduced capital costs. However, this assessment was based on using bio-oil for reforming and acknowledged uncertainty in pricing for co-products. Their analysis, at a 20% IRR, provided plant gate pricing of hydrogen from \$9.79-\$11.41/GJ. In the UT study, hydrogen production equipment  
15 represented 23% of the total capital equipment costs and utilized a \$4/GJ expense for methane. This cost represented ~50% of total expenses and ~45% of before tax profits. If we assume that other operational costs remain the same, with the increased cost of natural gas, the inside plant cost of renewable hydrogen would no longer be 2.4-2.8 times the costs from methane, but is approaching 1.6-1.9  
20 times. Since net profits were based on market price of nitrogen, then increases in natural gas prices will change total income in the model as well. For simplicity if we use \$7/GJ, then total income would increase 1.75x and expenses related to renewable hydrogen would roughly equal ~50% of before tax profits. Intra plant usage of renewable hydrogen (i.e. no storage or transport expense) becomes  
25 significantly more competitive at our current natural gas prices.

Another advantage comes from a review of traditional ammonia processing methods and how they compare to the ECOSS process. The UT study notes that due to unfavorable equilibrium conditions inherent in  $\text{NH}_3$  conversion, only 20-  
30 30% of the hydrogen is converted in a single pass. From the section in this paper on Production Chemistry Calculations, we determined that the ECOSS process could only utilize 31.6% of the hydrogen as we were limited by the total amount of char produced and the target 10% nitrogen loading. This means that it possible that a single pass  $\text{NH}_3$  converter could be used and the expense of separating and  
35 recycling unconverted hydrogen is eliminated. The 68.4% hydrogen is then

5 available for sale or use by the power company/fertilizer partnership. This shows that the ECOS process thus favors the inefficiencies of ammonia production and reduces costs inherent in trying to achieve high conversion rates of hydrogen.

10 With increased biomass utilization for energy and increasing demands for food production, the requirements for fertilization will increase. The restoration and return of micronutrients could allow substantive increases in overall soil amendment applications and the potential needs for nitrogen may not be such a limiting factor as was considered in the UT study. From a global systems view, the combination of topsoil restoration, desert reclamation, and the associated  
15 increases in biomass growth, could allow the economics to be driven not by C capture but rather by value creation of increased soil/crop productivity.

This concept of biomass energy production with carbon utilization may open the door to millions of tons of CO<sub>2</sub> being removed from industrial emissions while  
20 utilizing captured C to restore valuable soil carbon content. This process simultaneously produces a zero emissions fuel that can be used to operate farm machinery and provide electricity for rural users, agricultural irrigation pumps, and rural industrial parks. Future developments from the global research community will produce a range of value added carbon containing co-products  
25 from biomass. With this development and future use of inventions like this, both the producers of carbon dioxide and agricultural community have the capability to become a significant part of the solution to the global rise in greenhouse gas emissions while building sustainable economic development programs for agricultural areas in the industrialized and economically developing societies.

30 As illustrated in Fig. 1, a stream of dry chipped, pelletized or cut biomass in sizes determined by the type of pyrolyzer and biomass utilized 100 or carbonaceous material (renewable is best for carbon credit creation) is added to a pyrolysis, partial gasification, or thermolysis reactor 102. These reactors can be fast  
35 pyrolysis (and thus require smaller particles, or slow pyrolysis allowing larger

5 particle size but having larger dimensions to effect the same throughput. These  
can be downdraft, updraft, cross draft, fluid bed or rotating kilns. These systems  
come in many commercial designs and are well known to those skilled in the art.  
The ability to maintain good temperature control and control char removal  
temperatures are important. An inert heat source 103 provides a heat source for  
10 bringing the reactor and can help assist in maintaining the operating temperature  
well within the exothermic range for the material. Since each biomass has  
differences, there is no set rule, but most well designed pyrolysis units can operate  
with little external heat after startup and with limited oxygen present. The char  
removal will function best with an automated gate or star valve which discharges  
15 the char at optimal temperature ranges for the desired material. The higher  
temperature chars will release nutrients faster than lower temperature chars and  
according to the use and application of the fertilizer. However the range to insure  
maximum ammonia uptake will be less than 500C and above 350C. When  
dealing with any new biomass, adsorption rates should be tested to establish  
20 performance criteria. This can be done by pyrolysis of the new material across a  
range of pyrolysis temperatures using a small furnace. Those skilled in the art can  
measure adsorption of ammonia on char using a sampling bag (tedlar bag), with a  
standard concentration of ammonia, char and using an analytical ammonia  
detector. As raw materials will vary, these tests can insure a baseline performance  
25 in scrubbing as well as in fertilizer performance. The inert heat source can be one  
of many gas, flue gas, nitrogen, carbon dioxide, but gas should be chosen to be  
compatible with the hydrogen production system. In the case of hydrogen steam  
reforming, heat recovered from the reformer 106 can be used and then the  
reformer will use the steam in transferred with the pyrolysis gases 105 for  
30 hydrogen production. As the char reaches the optimal temperature it is discharged  
into a nonoxidative chamber or transfer unit 108. The char can be allowed to cool  
slowly or can be lightly sprayed with water as it is discharged. The char is then  
ground 111 to 0.5.-3mm. This will also vary according to the char materials.  
Chars made from grasses and lightweight biomass will crush easily to and create a  
35 larger percentage of smaller materials. These will agglomerate into bigger

5 particles later, so they can still be used with suitable baghouses. There is evidence that larger particles work just as effectively as small particles. The reason for this is unknown.

10 The hydrogen production system, 106 while shown as steam reforming followed by CO shift, this system can be any unit that produces hydrogen suitable for continued processing into ammonia. The preferred system for maximum atmospheric carbon reduction is one which uses biomass or renewably derived fuels and derives its energy from a carbon neutral or negative source. Gases 109 containing primarily hydrogen and CO<sub>2</sub> are separated using pressure swing  
15 adsorption 110 or other industry acceptable methods. The carbon dioxide 114 is greenhouse neutral at this point and can be release or used to replace 115 flue gas if there is no fossil fuel based carbon dioxide 123 available. When operated in this manner the energy derived has an even higher effective carbon negative accounting. Ammonia production 117 is shown as using the Haber process or  
20 other economically and industry accepted methods for ammonia production. At conditions needed to sequester .75 to 1.5 tons per hectare of carbon and provide sufficient charcoal to offer substantive plant response, a 10% nitrogen content is recommended. The resulting balance then points to 60-67% of the hydrogen produced will be available for sale. This lends to a configuration where 3  
25 locations feed one which is the capture and fertilizer production center. The others produce hydrogen and or energy and charcoal which is sent then to one location where all of its hydrogen is utilized.

30 The ammonia produced 118 is then saturated with water by bubbling ammonia through water 119. This reaction produces heat and the water levels need to be monitored and automatically maintained. The gas phase hydrated ammonia 120 is then allowed to enter a chamber 121 with the charcoal. This saturation will be sufficiently complete in 3-10 seconds, according to particle size. The concentrations added to the char will be equal to 1.1-1.5 mole of NH<sub>3</sub> per mole of



- 5 CO<sub>2</sub> in the flue gas sought to capture as NH<sub>4</sub>HCO<sub>3</sub>. Char 112 is added at the so as to achieve the desire nitrogen ratio:

$$\text{Charcoal Weight} = (1 - (\text{TargetNitrogen\%} * 79 / 14)) * \text{CapturedCO2moles} * 79$$

- 10 The amount of percentage SO<sub>x</sub> and NO<sub>x</sub> will be significantly lower than the number of moles of CO<sub>2</sub> sought and at these temperatures, the production of ammonium sulfate and ammonium nitrate will reduce to mandatory emission levels and will become part of the ECOS matrix increasing its value.
- 15 The saturate char 122 is then feed into a system, label here as a conversion cyclone, 124 where flue gases (with or without fly ash) 123 (at ambient temperature and pressure) can mix intimately and evenly also where the particles, once having completed the conversion of the adsorbed NH<sub>3</sub> to NH<sub>4</sub>HCO<sub>3</sub>, the particles are separated from particles which have not completed converted all of
- 20 their NH<sub>3</sub>. The gases 125 now scrubbed of emissions and most of the fly ash are sent for final particulate scrubbing. The charcoal fertilizer granules are discharged 126 as they reach the desired density set by the nitrogen percent. Optionally, the charcoal fertilizer can be 126 mixed with other nutrients 131, trace minerals, and optionally coat 132 the granules with the above nutrient, or plaster, or polymers,
- 25 or sulfur as known to those skilled in the arts, to give the particles longer and more precise 133 discharge rate, or a less expensive but effect soil amendment 134.

- Fig. 2 illustrates the design of a simple conversion cyclone system to demonstrate
- 30 the features described. Optimized charcoal 136 is gravity feed into a pipe between two valves 138 that allows the chamber 137 to be closed and a valve permits a gas stream of hydrated ammonia 135 to enter and saturate the material. The bottom valve of the two sealing the chamber is then opened allowing the saturated char to enter the 1.5 meter tall and a 50 cm diameter mechanically power cyclone. The
- 35 stainless cylinder has a variable speed motor 145 driving a plastic fan/rotor which

5 keeps the gas and particles held up in suspension. Two thirds of the way down is a discharge cyclone 142 with rotating gate 141 to control gas flows through the cyclone. The metered CO<sub>2</sub> rich gas stream 140 enters the cyclone, and in practice would discharge through the bottom where a glass sampling container 146 was located. A second glass sampling container 143 was located under the discharge  
10 cyclone. A gas sampling and discharge port 139 was located at the top of the system. Plexiglass view ports 147 allowed the suspended particles to be viewed as they moved down toward the discharge cyclone.

Fig. 3 illustrates conceptual design to remove CO<sub>2</sub> emissions in industrial  
15 combustion facilities such as a coal-fired power plant by flexible combinations of the synergic processes as described in this invention: the pyrolysis of biomass and or carbonaceous materials and ammonia scrubbing. This CO<sub>2</sub>-removal technology produces valuable soil amendment fertilizer products such as NH<sub>4</sub>HCO<sub>3</sub>-char that can be sold and placed into soil and subsoil terrains through intelligent agricultural  
20 practice. Therefore, this invention could serve as a potentially profitable carbon-management technology for the fossil energy industries and contribute significantly to global carbon sequestration.

Fig. 4 illustrates the expected benefits from use of the invention that combines the  
25 biomass pyrolysis and NH<sub>3</sub>-CO<sub>2</sub>-solidifying NH<sub>4</sub>HCO<sub>3</sub>-production processes into a more-powerful technology for carbon management. This invention provides benefits of carbon sequestration and clean-air protection by converting biomass and industrial flue-gas CO<sub>2</sub> and other emissions into mainly NH<sub>4</sub>HCO<sub>3</sub>-char products. The NH<sub>4</sub>HCO<sub>3</sub>-char products can be sold as a fertilizer and be placed  
30 into soil and subsoil earth layers as sequestered carbons, where they will also improve soil properties and enhance green-plant photosynthetic fixation of CO<sub>2</sub> from the atmosphere thus increasing biomass productivity and economic benefits.

The pyrolysis of biomass materials and the steam reforming of the off gases  
35 and/or pyrolysis liquids produces significant amounts of hydrogen and a solid char

5 product. Hydrogen, after separation, can be converted into ammonia using the industry standard Haber-Bosch process as the two reactions operate at the same temperature range. The ammonia when combined carbon dioxide ( $\text{CO}_2$ ) form ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ), with sulfur dioxide or nitrous oxide and a platinum and nickel catalyst will form  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . These which combined  
10 with  $\text{NH}_3$  will form as an intermediate of  $\text{NH}_4\text{HCO}_3$  and  $(\text{NH}_2)_2\text{CO}$  production process, to form additional fertilizer species,  $(\text{NH}_4)\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . The invention described here is the simultaneous production of hydrogen, its conversion into ammonia, a porous char, the combination of ammonia, and the flue gases of combustion or other high percentage sources of carbon dioxide and  
15 the porous char in order to deposition of nitrogen rich compounds in the pore structure of the carbonaceous material. The invention provides the use of this combined porous adsorbent char, enriched with nitrogen compounds, a slow release design coating from plaster, polymer and/or sulfur, for a slow release fertilizer/soil amendment with which is a novel method for sequestering large  
20 amounts of carbon from the atmosphere. Char makes a perfect media for storing significant quantities of compounds. The combination of nitrogen compounds created in and on the carbon can produce a slow release nitrogen fertilizer with many advantages over traditional ammonium nitrate, urea or liquid ammonia. One of these is that it is less reactive reducing the risk of it being used a  
25 compound for making explosives.

Since both the bicarbonate  $\text{HCO}_3^-$  of  $\text{NH}_4\text{HCO}_3$  and the elementary carbon (C) of the char materials are nondigestible to soil bacteria, they can be stored in soil and subsoil earth layers as sequestered carbons for many years. Therefore, a  
30 combined  $\text{NH}_4\text{HCO}_3$ -char product can not only provide nutrients (such as  $\text{NH}_4^+$ ) for plant growth, but also has the potential to fully utilize the capacity of soil and subsoil earth layers to store both inorganic carbon (such as  $\text{HCO}_3^-$ ) and organic elementary carbon (C). Urea  $(\text{NH}_2)_2\text{CO}$  can also be combined with the char materials to form a similar product. However, the urea production process  
35 generally costs some more energy and has less capacity to solidify  $\text{CO}_2$  than the

5 CO<sub>2</sub>-solidifying NH<sub>4</sub>HCO<sub>3</sub> production process (U.S. Patent No. 6,447,437B1).  
The char materials are also mixable with other nitrogen fertilizer species such as  
NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)SO<sub>4</sub>, but those mixtures would not have the benefits of  
providing bicarbonate (HCO<sub>3</sub><sup>-</sup>) to soils. Therefore, the combined NH<sub>4</sub>HCO<sub>3</sub>-char  
product is preferred in realizing the maximal carbon-sequestration potential in soil  
10 and subsoil earth layers (Figs. 1 and 2).

Furthermore, the combined NH<sub>4</sub>HCO<sub>3</sub>-char product has synergistic benefits.  
First, the char particles can be used as catalysts (providing more effective  
nucleation sites) to speed up the formation of solid NH<sub>4</sub>HCO<sub>3</sub> particles in the CO<sub>2</sub>-  
15 solidifying NH<sub>4</sub>HCO<sub>3</sub> production process, thus enhancing the efficiency of the  
CO<sub>2</sub>-solidifying technology. Second, the char materials are generally alkaline in  
pH because of the presence of certain mineral oxides in the ash product. The pH  
value of a typical char material is about 9.8. This alkaline material may not be  
favorable for use in alkaline soils such as those in the western United States while  
20 it is very suitable for use in acidic soils such as those in the eastern United States.  
However, use of NH<sub>4</sub>HCO<sub>3</sub> can neutralize the alkali of the char materials. When  
the char materials are mixed with NH<sub>4</sub>HCO<sub>3</sub> of equal weight, the pH of the  
product becomes much better (closer to neutral pH 7). As illustrated in Table 1,  
the pH value of the NH<sub>4</sub>HCO<sub>3</sub>-char mixture is 7.89, which is significantly lower  
25 (better) than that of the char material (pH 9.85). Therefore, this type of  
NH<sub>4</sub>HCO<sub>3</sub>-char combined fertilizer will be able to be used in alkaline soils, in  
addition to pH neutral and acidic soils. This type of NH<sub>4</sub>HCO<sub>3</sub>-char fertilizer can  
be produced either by the char particle-enhanced NH<sub>3</sub>-CO<sub>2</sub>-solidifying NH<sub>4</sub>HCO<sub>3</sub>  
production process (Fig. 3) or by physically mixing NH<sub>4</sub>HCO<sub>3</sub> with char  
30 materials. Figure 4 presents photograph of the NH<sub>4</sub>HCO<sub>3</sub>-char fertilizer samples  
that were created by char particle-enhanced NH<sub>3</sub>-CO<sub>2</sub>-solidifying NH<sub>4</sub>HCO<sub>3</sub>  
production process [marked as "treated char"] and by a physical mixing of  
NH<sub>4</sub>HCO<sub>3</sub> and char [marked as "NH<sub>4</sub>HCO<sub>3</sub>-char mixture (50%/50%W)"].  
Depending on the amount of NH<sub>4</sub>HCO<sub>3</sub> deposited onto the char particles by char  
35 particle-enhanced NH<sub>3</sub>-CO<sub>2</sub>-solidifying NH<sub>4</sub>HCO<sub>3</sub> production process, the treated

5 char has a pH value of 8.76 in this particular sample. The pH of the product can be further improved by deposition more  $\text{NH}_4\text{HCO}_3$  onto the char particles by the process.

10 When the  $\text{NH}_4\text{HCO}_3$ -char product is applied into soil, it can generate yet another synergistic benefit. For example, in the western parts of China and the United States where the soils contains significantly higher amount of alkaline earth minerals and where the soil pH value is generally above 8, when  $\text{NH}_4\text{HCO}_3$  is used alone, its  $\text{HCO}_3^-$  can neutralize certain alkaline earth minerals such as  $[\text{Ca}(\text{OH})]^{+}$  and/or  $\text{Ca}^{++}$  to form stable carbonated mineral products such as  $\text{CaCO}_3$   
15 that can serve as a permanent sequestration of the carbon. As more and more carbonated earth mineral products are formed when  $\text{NH}_4\text{HCO}_3$  is used repeatedly as fertilizer for tens of years, some of the soils could gradually become hardened. This type of "soil hardening" has been noticed in some of soils in the western part of China where  $\text{NH}_4\text{HCO}_3$  has been used as a fertilizer for over 30 years. It is also  
20 known that this type of soil "hardening" problem could be overcome by application of organic manure including humus. Char is another ideal organic material that can overcome the "soil hardening" problem because of its soft, porous, and absorbent properties. Therefore, co-use of  $\text{NH}_4\text{HCO}_3$  and char materials together can allow continued formation of carbonated mineral products  
25 such as  $\text{CaCO}_3$  and/or  $\text{MgCO}_3$  to sequester maximal amount of carbons into the soil and subsoil terrains while still maintaining good soil properties for plant growth.

30 Another embodiment of the invention can be to also add other nutrients to the carbon. The material itself contains trace minerals needed for plant growth. Adding phosphorus, calcium and magnesium can augment performance and create a slow release micro nutrient delivery system.

35 Another embodiment of the invention can include the processing of the carbon to produce very large pore structures. The material can be used as an agent to

5 capture watershed runoff of pesticides, and herbicides. By adding a deposition of various materials (example: gaseous iron oxide), the material can be used to capture such compounds as phosphorus from animal feedlots.

Another embodiment for the invention is to use standard industrial processes well  
10 known to those skilled in the arts, to use the hydrogen produced, combined with air and other free nitrogen present in the production process to create the ammonia that will be used as the nitrogen source material.

Based on market demands, these products can be further combined with other  
15 fertilizer species such as potassium, magnesium, ammonium sulfate, ammonium nitrate, and micro mineral nutrients such as iron and molybdenum to make more-nutrient-complete compound fertilizers.

To assist an appreciation by those of skill of the art for the scope of exemplary  
20 embodiments of the present invention, the Applicants have identified within the body of this technical specification certain publications relevant to the technical field of the present invention. Applicants have used an identifier of the format "Author(s)/Publication year" to provide a readily recognizable identifier for these references. A complete listing of the identified references is provided below in  
25 Table 3.

### Table 3

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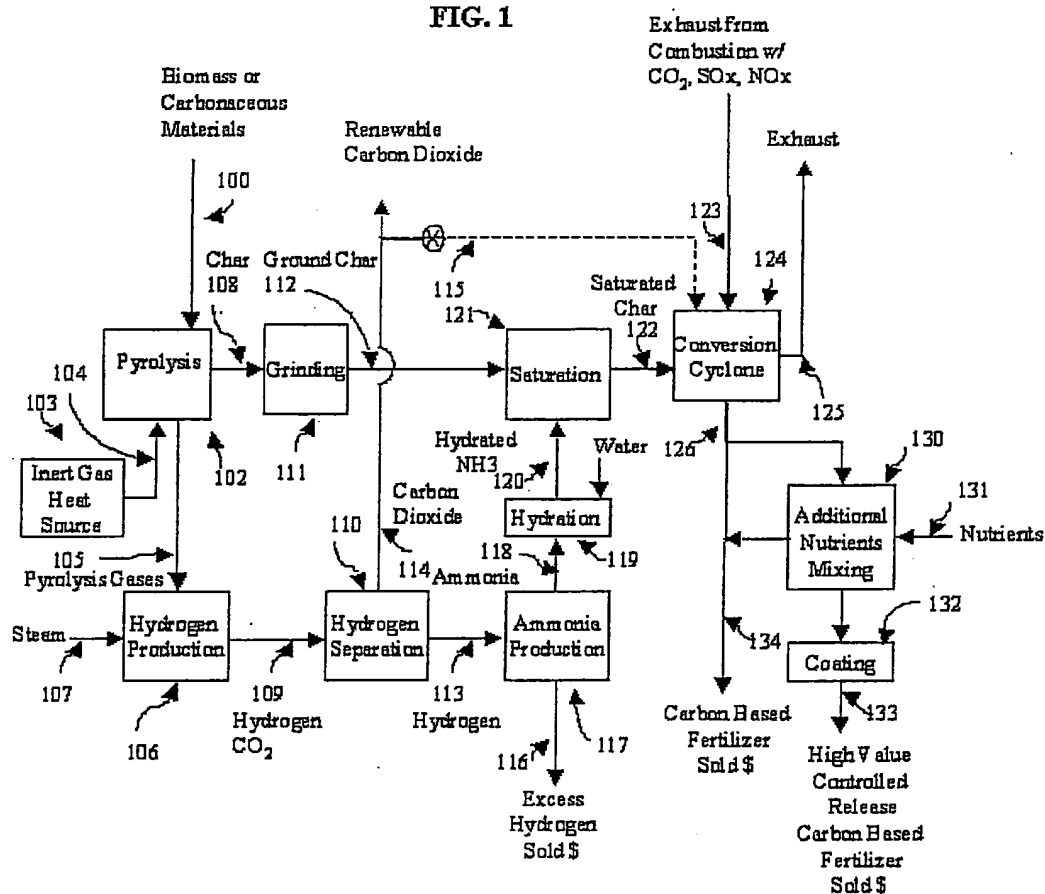
5    **Claims**

1. A process for the pyrolysis of biomass and other carbonaceous materials releasing a pyrolytic gas high in volatile organic compounds and producing a solid carbon charcoal residue.  
10
2. The process as in Claim 1 where the temperature of the charcoal is managed to such that its does not exceed the temperature range between 350C where 500C for more than 2 minutes to maximize the formation of surface acids groups and preferential adsorption of bases which include ammonia,  
15
3. The process as in Claim 1 where the temperature of the resulting char particles exceeds 500C and is further heated or allowed to oxidized where the temperature remains above 600C for greater than 10 minutes to minimize the production of surface acids groups.  
20
4. The process as in Claims 1, 2 and 3 wherein the residue is further processed under various conditions, including but not limited to pressure, mechanical actions, heat, steam, oxygen, acid, carbon dioxide, addition of fertilizer components, such as potassium, magnesium, ammonium sulfate,  
25 ammonium nitrate, micro mineral nutrients such as iron molybdenum minerals, to optimize it for specific applications as an adsorbent and carrier of other materials.
- 30 5. The process as in Claim 1, where in the gas is further processed using ceramic membranes to the convert and extract a purified hydrogen stream, or by using steam reforming or catalytically reforming of the pyrolysis or synthesis gas to produce a mixture gases including hydrogen, carbon monoxide, methane and carbon dioxide and where the carbon monoxide is  
35 produced it is converted through a high temperature or low temperature

- 5 catalytic CO water shift reaction to hydrogen where hydrogen and carbon dioxide are the major components of the resulting gas.
6. The process as in Claim 5, for separating the any unpurified hydrogen from carbon dioxide, nitrogen or other parasitic gases using standard industrial techniques, such as pressure swing adsorption, or membrane separation.
- 10 7. A process in accordance with Claims 1, 5 and 6, where the combination of the hydrogen and air are used in standard industrially accepted techniques to produce ammonia or ammonium nitrate or other nitrogen compounds typical to those industry practices.
- 15 8. The process in accordance with Claims 2 and 4, whereby all or a portion of the solid charcoal and ammonia, and water is injected or brought into intimate contact with the off-gas stream of a combustion or other process where such gas stream has a concentration of carbon dioxide, sulfur dioxide and nitrous oxide and where there is a desire to reduce the discharge of these materials into the atmosphere.
- 20 9. The process in accordance with Claims 3 and 4, whereby all or a portion of the solid charcoal, and ammonia, and water is injected or brought into intimate contact with the off-gas stream of a combustion or other process where such gas stream has a concentration of carbon dioxide, sulfur dioxide and nitrous oxide and where there is a desire to reduce the discharge of these materials into the atmosphere.
- 25 30 10. The process in accordance with Claims 8 and 9, where the charcoal residue and ammonia, water and off gases are held in intimate contact for at least 5 seconds.
- 35

- 5 11. The process as in Claim 10 wherein the chemical reaction will allow ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) to be formed in the charcoal pores and onto its surface to produce  $\text{NH}_4\text{HCO}_3$ - charcoal fertilizers.
- 10 12. The process as in Claim 10 wherein the chemical reaction also allows the formation of ammonium salts of nitrogen oxides and sulfur dioxide to be formed in contact with  $\text{NH}_4\text{HCO}_3$ -charcoal fertilizers.
- 15 13. The creation of a slow release sequestering soil amendment fertilizer to be combined with materials used by plant growth and depositing those materials inside the internal pore structures of the carbon residue making a solid powder and or granular material suitable for large scale agricultural applications.
- 20 14. A process in accordance with Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13 where those compounds beneficial for plant growth are created or adsorbed onto the internal pore structure of the carbon residue creating a material which provides a slow release of the compounds.
- 25 15. A process in accordance with Claim 13, and a coating is used to facilitate the handling, flow and added control of the rate of release of those compounds, and where such materials as are commonly used to create coatings such as but not limited to gypsum, plaster, sulfur, polymers as materials which dissolve or create a permeable layer when placed in the soil.
- 30 16. The use of a material as a soil amendment and fertilizer made with the processes described in Claims 1 through 11 and creating those materials as described in Claims 11, 12 or 13.

FIG. 1



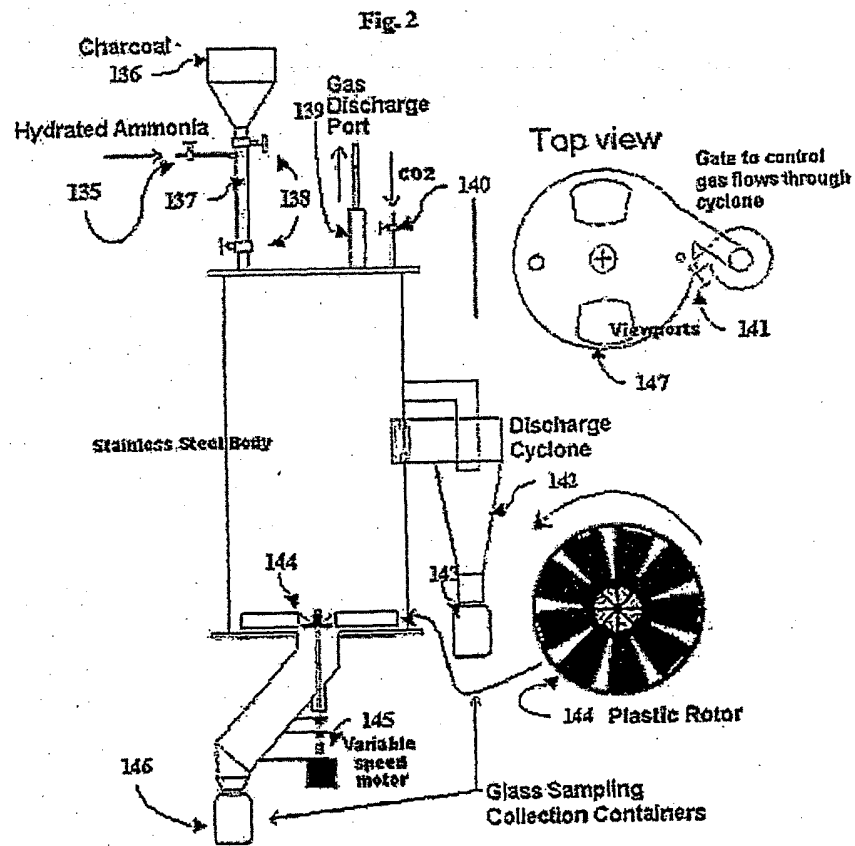




Fig. 3

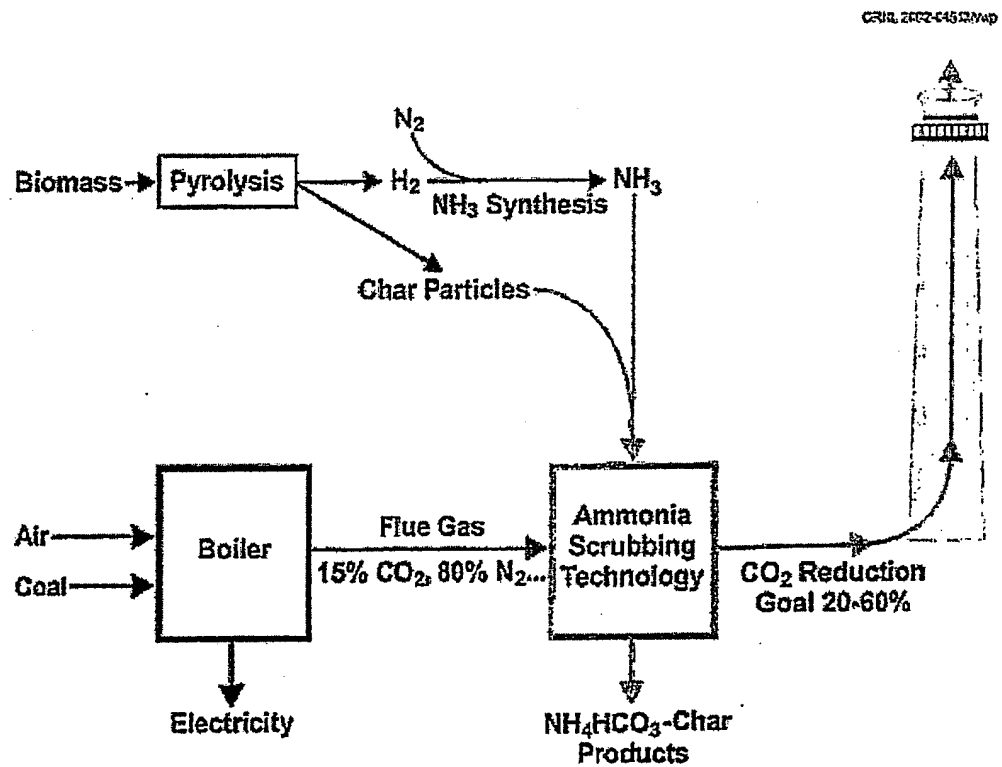
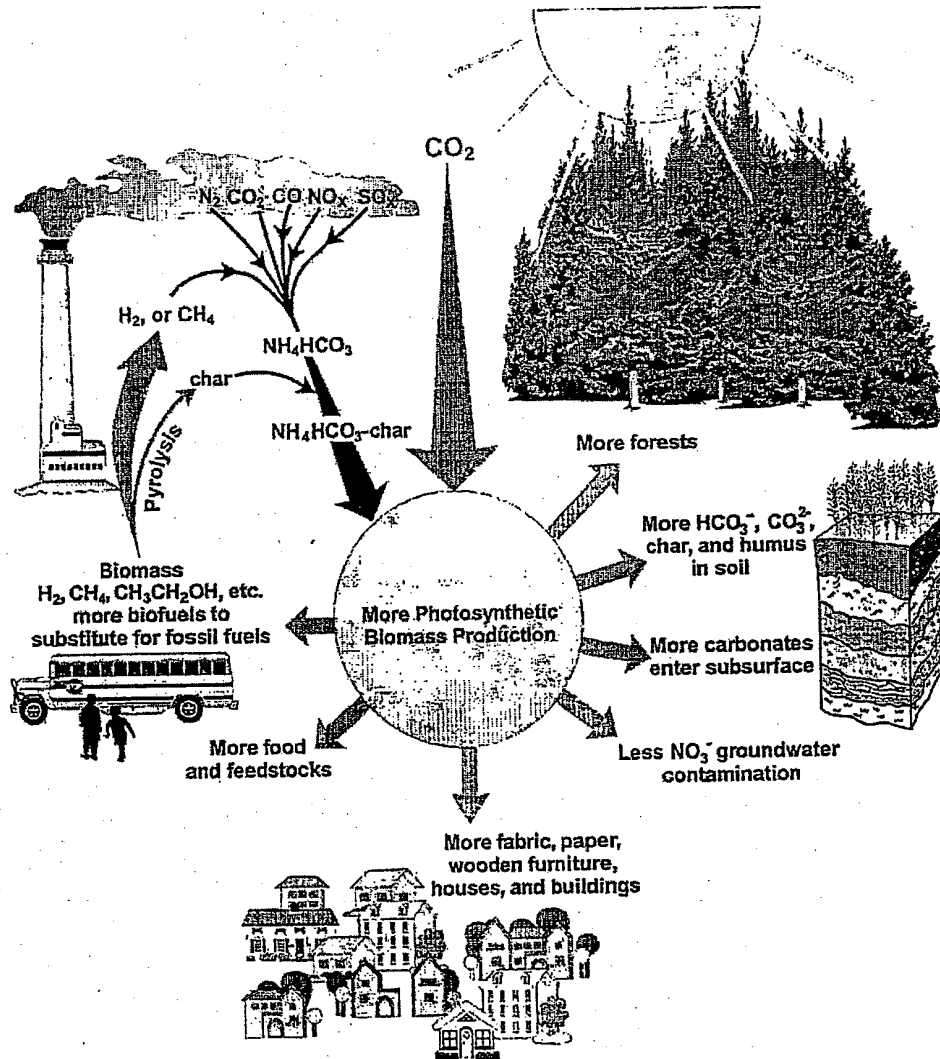


Fig. 4

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